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# Neutron diffraction as a probe of liquid and glass structures under extreme conditions

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Neutrons provide a unique tool for probing the structure of liquid and glassy matter, and deliver information that cannot be obtained from other experimental techniques. Advances in neutron diffraction instrumentation and measurement protocols now make it possible to measure the structure of these disordered materials under extremes of high temperatures or high pressures. Here, we consider the use of aerodynamic levitation with laser heating to explore the structure of glass-forming oxide melts at high temperatures, and the use of a Paris-Edinburgh press to investigate the mechanisms of density-driven network collapse for glassy materials in the gigapascal (GPa) pressure regime.

## Introduction

The structural complexity of liquid and glassy materials makes for a challenging field of research to which neutron diffraction has made seminal contributions, especially when it has been combined with the isotope substitution method [1, 2]. The atomic-scale disorder of these materials leads to diffuse scattering, such that experiments requiring small samples and complex sample environments must be carefully designed if the sample scattering is to be distinguished from the container and background scattering. Aerodynamic levitation with laser heating offers a container-less method for investigating the structure of a wide variety of high-temperature liquids [3], but the small levitated sample is partially obscured from an incident neutron beam by the material of the levitator's nozzle (Fig. 1). The Paris-Edinburgh press provides a means for accessing pressures in the GPa regime [4], but a small sample must be contained within a gasket such that scattering from the gasket and anvils of the press cannot be avoided [5]. However, as will be illustrated in the following, it is possible to circumvent these experimental challenges. Indeed, it is even possible to apply the method of neutron diffraction with isotope substitution (NDIS) to provide site-specific information on a material's structure under extreme conditions [1, 2]. Here, diffraction patterns are measured for two or more samples that are identical in every respect, except for the isotopic enrichment of one or more of the chemical species. These patterns are then subtracted, thus reducing the number of overlapping pair-correlation functions that contribute towards a single diffraction pattern.

## Structure of high-temperature liquids by neutron diffraction with isotope substitution

$\text{CaAl}_2\text{O}_4$  is one of a family of glass-forming materials that are widely studied because of their geological and technological relevance. The laser-heated aerodynamic-levitation technique has been combined with the NDIS method using Ca isotopes in order to measure the structure of a single levitated liquid droplet of  $\text{CaAl}_2\text{O}_4$  at a temperature of 1973 K [6]. The NDIS method has also been applied to measure the glass structure at ambient temperature [6]. The experiments employed the diffractometer D4c at the Institut Laue-Langevin (ILL), and the measured real-space difference functions  $\Delta G_{\text{Ca}}(r)$  and  $\Delta G_{\mu\mu}(r)$  are shown in Fig. 2.  $\Delta G_{\text{Ca}}(r)$  involves only the Ca-Ca and

Ca- $\mu$  pair-correlation functions, where  $\mu$  denotes either an Al or O atom, whereas  $\Delta G_{\mu\mu}(r)$  involves only the  $\mu$ - $\mu$  pair-correlation functions. The first peaks in  $\Delta G_{\text{Ca}}(r)$  and  $\Delta G_{\mu\mu}(r)$  correspond to the Ca-O and Al-O nearest-neighbours, respectively. The diffraction results are compared to those obtained by using molecular dynamics with a polarisable ion model. It is found that significant structural changes occur on vitrification of this fragile glass-forming material on both the local and intermediate length scales. For instance, edge-sharing Ca-centred polyhedra occur in the liquid phase and become far more numerous as the system is quenched to form a glass (Fig. 3). Thus, although glass is often used as a proxy for the corresponding liquid in order to explore possible structural configurations at extreme conditions, these configurations may not be representative of the liquid phase in so-called ‘fragile’ glass-forming systems, a taxonomy that includes  $\text{CaAl}_2\text{O}_4$  and a range of magma-related materials [6].

### Structure of silica glass by *in situ* high-pressure neutron diffraction

Silica is the canonical network glass, whose pressure-dependent behaviour is often used as a reference for silicate materials that have geophysical relevance. Figure 4 shows the pressure dependence of the total structure factor  $S(Q)$  as measured by neutron and x-ray diffraction, where the information provided by these techniques is complementary: The relative values of the coherent neutron scattering lengths and x-ray form factors for Si and O ensure that the neutron and x-ray  $S(Q)$  functions are more sensitive to the O and Si atom pair-correlation functions, respectively [7]. For example, at ambient pressure the neutron  $S(Q)$  function has a peak at a scattering vector  $Q \sim 2.9 \text{ \AA}^{-1}$  that is absent from the x-ray  $S(Q)$  function. The neutron diffraction experiments were performed using a Paris-Edinburgh press with (i) an in-plane scattering geometry and neutron absorbing BN anvils on the diffractometer D4c (ILL) at pressures up to 8.2 GPa [8], or (ii) a transverse scattering geometry and sintered diamond anvils on the diffractometer PEARL (ISIS) at pressures up to 17.5 GPa [9]. The sample volumes in these diffraction experiments were about 91 and 34 mm<sup>3</sup>, respectively [5]. The diffraction data are compared to those obtained from molecular dynamics simulations using the Tangney-Scandolo interaction model which incorporates anion polarisation terms.

The results show that the transformation from a network of  $\text{SiO}_4$  tetrahedra to a network of  $\text{SiO}_6$  octahedra proceeds via the formation of five-fold coordinated Si atoms. In particular, the application of pressure leads to a reduction in size of the primitive rings that are formed by linked Si-centred motifs, a reduction that can be understood quantitatively in terms of a newly developed ‘zipper’ mechanism for ring closure [7]. The ring in Fig. 5 is deemed to be ‘primitive’ because it cannot be decomposed into smaller rings. When pressure is applied, the ring closes when silicon atom  $\text{Si}^{\text{I}}$  forms an additional bond with an intra-ring oxygen atom  $\text{O}^{\text{I}}$ , thus increasing the  $\text{Si}^{\text{I}}$  coordination number from four to five and the  $\text{O}^{\text{I}}$  coordination number from two to three. With increasing density, a further ring closure event then takes place at an adjacent site to create another over-coordinated silicon atom  $\text{Si}^{\text{II}}$  along with another over-coordinated oxygen atom  $\text{O}^{\text{II}}$ . The close proximity of these ring closure events helps to preserve locally the glass stoichiometry and, because the Si and O atoms are charged, this acts in a direction that helps to conserve local charge neutrality.

### Structure of high-pressure glasses by neutron diffraction with isotope substitution

$\text{GeSe}_2$  is a prototypical chalcogenide glass-forming system in which the topological and chemical ordering contrasts to that found in typical amorphous oxides. The structural information obtained on this system from conventional neutron and x-ray diffraction experiments is almost identical

because of the similarity between the coherent neutron scattering lengths of Ge and Se of natural isotopic abundance, and the similarity between the x-ray form factors for these elements. It is therefore desirable to obtain site-specific structural information, where the NDIS method with Ge and/or Se isotopes offers an excellent way forward [10]. This method has been used to explore the structure of GeSe<sub>2</sub> glass at pressures up to 8.2 GPa, and the resultant difference functions  $\Delta F_{\text{Ge}}(Q)$  and  $\Delta F_{\text{Se}}(Q)$  are shown in Fig. 6 [11]. These functions contain information solely on the Ge and Se pair-correlation functions, respectively, and were measured by using the diffractometer D4c (ILL) following the methodology developed in Ref. [12]. Conventional neutron diffraction has also been used to measure the structure of GeSe<sub>2</sub> glass at pressures up to 16.1 GPa, and the pressure-dependent structure of this material has been modelled by using first-principles molecular dynamics [11].

The results give an ambient pressure network that is built predominantly from corner and edge sharing Ge-centred tetrahedra, where Ge and Se are four-fold and two-fold coordinated, respectively, and the chemical ordering is broken by the appearance of Ge-Ge and Se-Se homopolar bonds [10, 11]. As the pressure is increased to ~8.5 GPa, the edge-sharing tetrahedra persist in substantial numbers and the mean coordination numbers of Ge and Se remain unchanged. At larger pressures, a mediating role is found for homopolar bonds in the appearance of higher-coordinated Ge and Se atoms. The persistence of edge-sharing configurations and role played by homopolar bonds are likely to be generic features of the densification processes in other chalcogenide glasses.

## Conclusions

The results presented above highlight the quality of information that can now be gained on the structure of liquid and glassy materials under extreme conditions from *in situ* neutron diffraction experiments. There is much to look forward to as the methodology is improved to enable the structure and properties of disordered materials to be explored over a broader range of state conditions.

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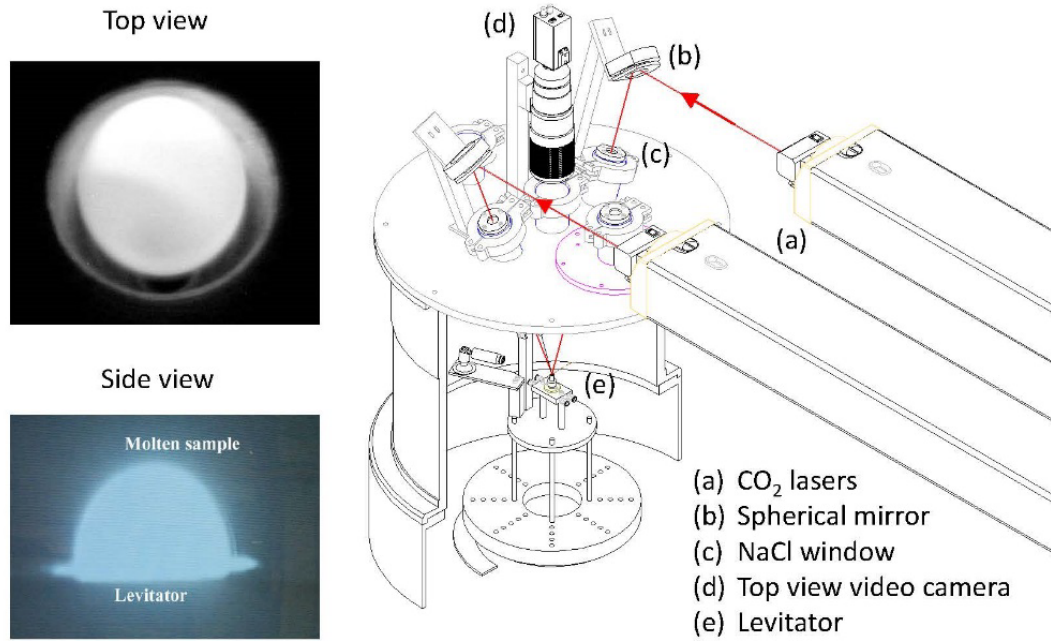


Fig. 1. Schematic of an aerodynamic levitation experiment as performed using the D4c diffractometer at the ILL. A small spherical sample of diameter 2-3 mm is levitated by the gas flow through a conical nozzle, and is heated by CO<sub>2</sub> lasers, where the laser beams enter the diffractometer bell jar via NaCl windows. The images to the left show a molten sample as viewed from both its top and its side. In the latter, the bottom of the sample is obscured by the nozzle material. (Figure courtesy of Louis Hennes, Orléans).

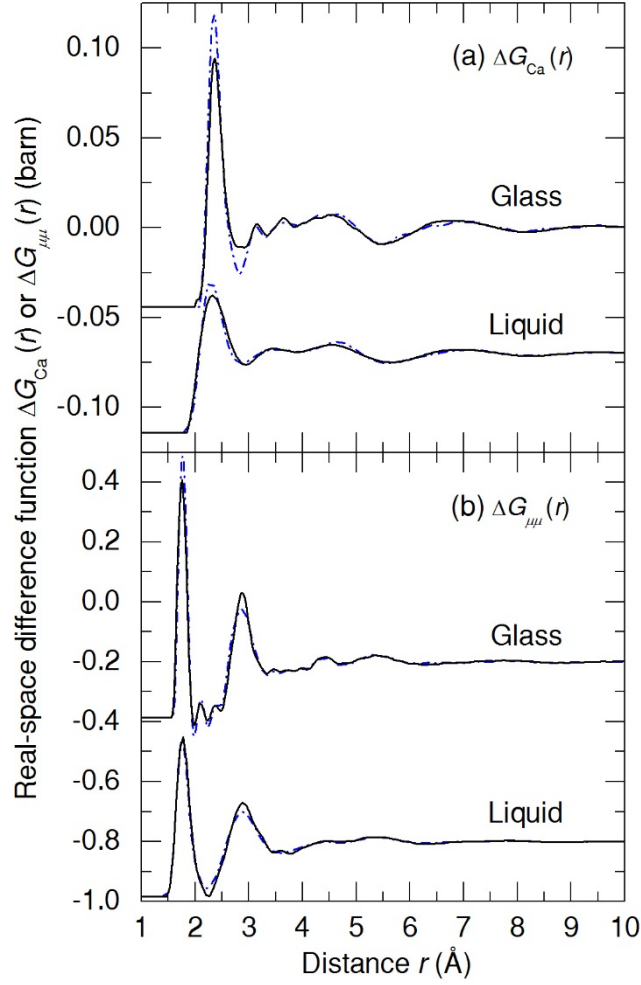


Fig. 2. The difference functions (a)  $\Delta G_{\text{Ca}}(r)$  and (b)  $\Delta G_{\mu\mu}(r)$  as (i) measured for a single droplet of liquid  $\text{CaAl}_2\text{O}_4$  of diameter 2.54 mm at a temperature of 1973 K or for a single bead of glassy  $\text{CaAl}_2\text{O}_4$  of diameter 3.18 mm at room temperature (solid curves); and (ii) modelled by using molecular dynamics (chained curves) [6].  $\Delta G_{\text{Ca}}(r)$  has contributions from the Ca-Ca and Ca- $\mu$  pair-correlation functions, where  $\mu$  denotes either an Al or O atom, whereas  $\Delta G_{\mu\mu}(r)$  has contributions from the  $\mu$ - $\mu$  pair-correlation functions alone.

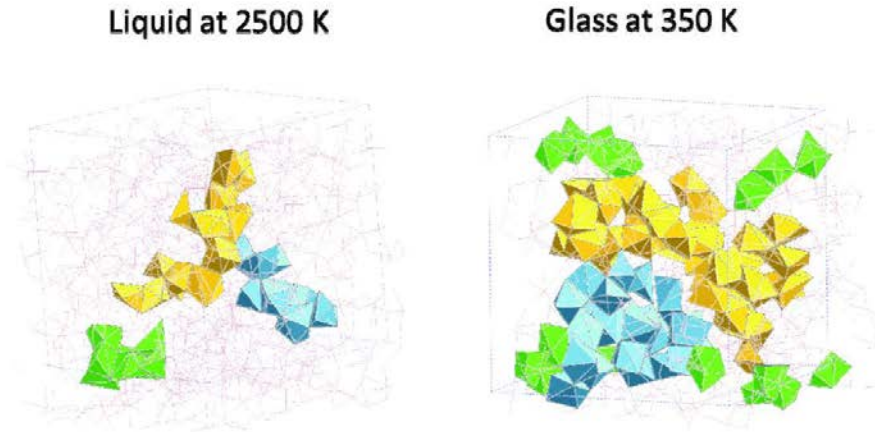


Fig. 3. Snapshots illustrating the largest clusters of edge-sharing Ca-centred polyhedra in molecular dynamics simulations of liquid and glassy  $\text{CaAl}_2\text{O}_4$  at temperatures of 2500 K and 350 K, respectively [6].



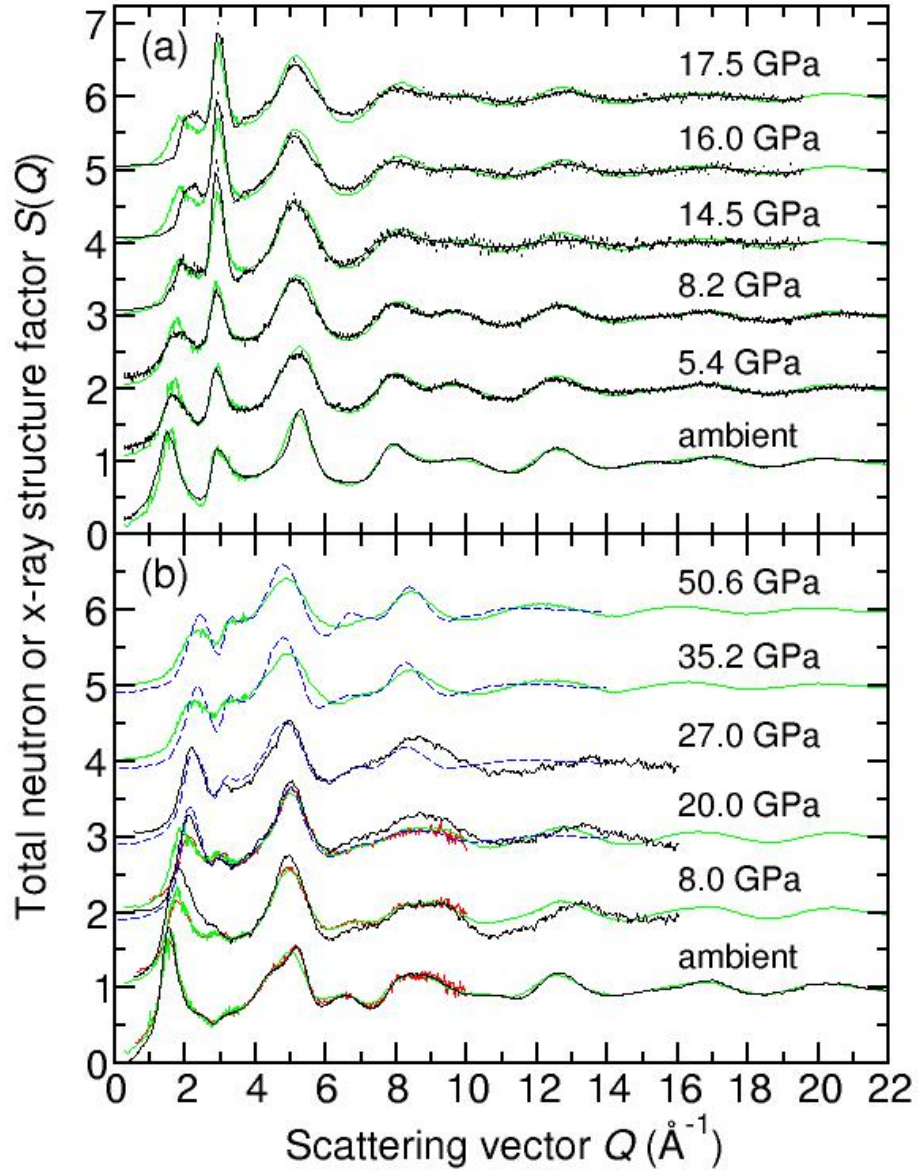


Fig. 4. The pressure dependence of the (a) neutron and (b) x-ray total structure factors  $S(Q)$  as measured in diffraction experiments on  $\text{SiO}_2$  glass under compression at room temperature [7]. The solid light (green) curves give the results obtained from molecular dynamics simulations, and the other curves give the experimental results.



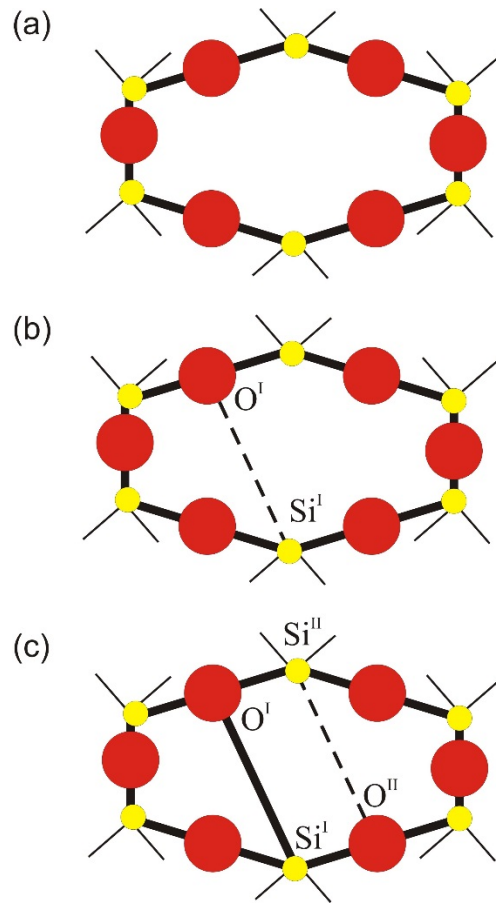


Fig. 5. Schematic of a series of ring closure events in  $\text{SiO}_2$  glass where the Si atoms are small (yellow) circles and the O atoms are large (red) circles [7]. The initial ring shown in (a) is closed by the formation of a bond between the  $\text{Si}^{\text{I}}$  and  $\text{O}^{\text{I}}$  atoms in (b), and is then closed again by the formation of a bond between the  $\text{Si}^{\text{II}}$  and  $\text{O}^{\text{II}}$  atoms in (c). At each stage in this ring-closure process, the existing Si-O bonds within a ring are shown by solid thick lines and the new Si-O bond is shown by a broken line. The remainder of the Si-O bonds are indicated by solid thin lines.

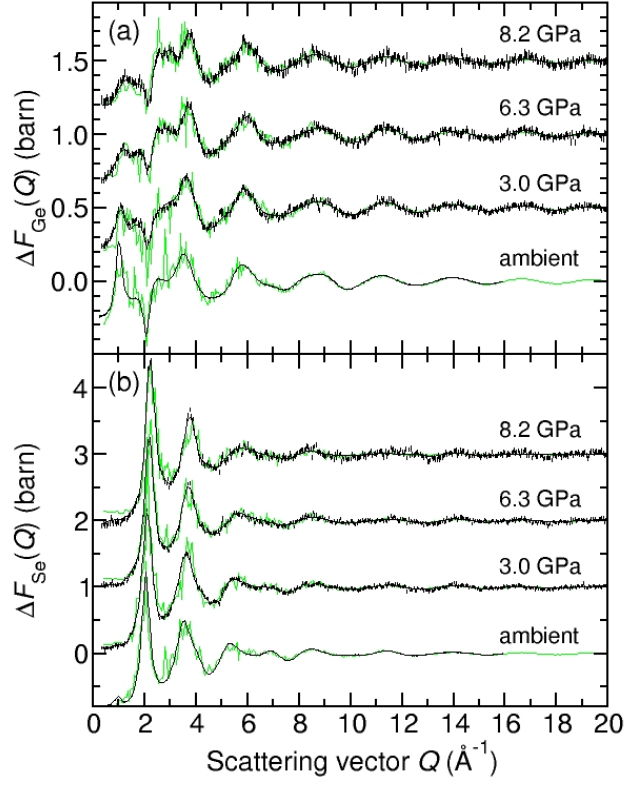


Fig. 6. The pressure dependence of the difference functions (a)  $\Delta F_{\text{Ge}}(Q)$  and (b)  $\Delta F_{\text{Se}}(Q)$  for  $\text{GeSe}_2$  glass, as measured by using NDIS (dark curves with vertical error bars) or simulated by using first-principles molecular dynamics (light (green) curves) [11].